

DETERMINATION OF CALCIUM, BARIUM, ZINC, SULFUR AND PHOSPHORUS
IN LIQUID HYDROCARBONS BY X-RAY FLUORESCENCE USING THE
CORRECTED INTENSITIES METHOD

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16. Abstract In the case of uniform liquid solutions such as doped oils and additives, the method of corrected intensities by double determination at two dilution ratios as recommended by R. Tertian theoretically makes it possible completely to eliminate the solubility matrix effect. This method requires no assumptions as to the nature of the sample studied and, contrary to the classical "weighting" method, involves the use of a light solvent which makes it possible to obtain optimum conditions of fluorescent intensity.			
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INTRODUCTION

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The cost and time expenditure for determination of mineral elements in hydrocarbon compounds by chemical methods led us to consider the determination of these elements by x-ray fluorescence. The main difficulty of this method lies in the preferential absorption, for the radiation of the element measured, of other elements in varying concentrations. We have studied several methods of correction and have developed that which seemed to us to be both the most widely applicable and the simplest to use.

The dilution method, which tends to render the absorption of atoms in the solute negligible in comparison to that of the atoms in the solvent, has not yielded satisfactory results. Although the dilution of doped oils with paraffin oil by a factor of ten furnished correct determinations for phosphorus and sulfur, this type of dilution was found inadequate in the case of heavier elements such as barium, calcium and especially zinc. More extensive dilution of the sample undergoing analysis, which is theoretically possible, is unacceptable in practice due to the increased error resulting from preparation and the decrease in sensitivity, for light elements in particular. In the case of additives, where the elements to be measured occur in higher concentrations, dilution by a factor of 50 in paraffin oil permitted the complete elimination of matrix effect for all elements with the exception of zinc, for which significant anomalies occur when the barium and calcium concentrations are varied. Due to these results, this method was set aside. /851

The internal standard method [1], since this standard could be predicted, permitted integral correction of the matrix effects. For

*Numbers in the margin indicate pagination in the foreign text.

oils and additives (the latter being diluted by a factor of 20 in paraffin oil), a lead salt may be used as an internal standard for the determination of zinc by a comparison of the ZnK_{α} and PbL_{α} rays, and for determination of sulfur by comparison of the SK_{α} and PbM_{α} rays. Moreover, a tin salt may be used as an internal standard for determination of barium (BaL_{α} , SnL_{β}) and calcium (CaK_{α} , SnL_{α}). Phosphorus, whose response is less sensitive to variations in opposition, can be measured directly. The same is true, to a lesser degree, for sulfur (Fig. 1). This method offers the additional advantage of making an integral correction for the systematic error of the test assembly, for each element to be measured, corresponding to a wavelength extremely close to the wavelength of determination. In addition, the elements added as internal standards must be absent from the products to be analyzed. These requirements necessitate extremely long and complex preliminary procedures which were incompatible with the simple, fast method which was proposed to develop.

The method of intensity correction by double determination at two dilution ratios [6] recommended by R. Tertian under the name "double dilution method," which we have applied here to doped oils and to additives, has been found the most attractive from the standpoint of both wide theoretical applicability and simplicity of use.

The purpose of this preliminary study was to check the validity of the assumptions which have been found justified in the case of solid solutions [3,4] and that of liquid solutions, in which the matrix effect is especially great. It was our basic intention to obtain the correction for matrix effect by comparing the curves of the measured intensity variations and corrected intensity variations as a function of concentration.

I. Corrected Intensity Method by Double Determination at Two Dilution Ratios: Summary of Procedure.

Drawing on the articles cited as references, especially Ref. [5] and [6], and considering our specific practical problem, we

can summarize the basics of the method in the following manner.

In the first place, it is assumed that the samples are strictly homogeneous ones in which the matrix effects are essentially due to differences in absorption. The reinforcement or enhancement effects, if there are any, are assumed to be included in "negative" absorption phenomena. In addition, it is assumed that the primary radiation, which is generally polychromatic, can be considered as an equivalent monochromatic radiation for the samples to be compared.

The general theory thus indicates that the fluorescent intensity of a homogeneous sample E containing a fluorescent element A in a concentration c_A is in the form:

$$I_{A_1} = C \cdot \frac{c_A}{e' + e} \quad (1)$$

in which C is a constant and e' and e denote the mass absorption coefficients of the sample in regard to the equivalent primary radiation (λ) and the fluorescent radiation of A (λ_A), respectively. We will term the sum of the parameters ($e' + e$) the resultant of absorption coefficient of the sample.

If the sample E is now dissolved, at a concentration x , in an appropriate solvent F [concentration(1 - x)], one obtains a new homogeneous sample E_2 in which the concentration of the fluorescent element is xc_A and whose resultant absorption coefficient, according to the law of additivity, is given by the expression:

$$x(e + e') + (1 - x)(f + f')$$

denoting the absorption parameter of the pure solvent by f' and f . By virtue of equation (1), the fluorescent intensity of the new sample will therefore be:

$$I_{A_2} = C \cdot \frac{xc_A}{x(e' + e) + (1 - x)(f' + f)} \quad (2)$$

If between equations (1) and (2) one eliminates the factor ($e' + e$) characterizing the matrix of the initial sample, by rearrangement one obtains the equation:

$$\frac{1-x}{x} \cdot \frac{I_{A_1} \cdot I_{A_2}}{I_{A_1} - I_{A_2}} = \frac{C}{f' + f} \cdot c_A \quad (3)$$

which shows that the combination of the two measurements:

$$I'_{E_1} = \frac{I_{E_1} \cdot I_{E_2}}{I_{E_1} - I_{E_2}} \cdot \frac{1-x}{x} \quad (4)$$

is independent of the matrix and directly proportional to the concentration sought c_A .

For this reason, I'_{E_1} is termed the "corrected intensity" for sample E_1 . The correlation of equation (3), written in the form:

$$I_{E_1} = \frac{C}{f' + f} \cdot c_A \quad (5)$$

and equation (1):

$$I_{E_2} = \frac{C}{e' + e} \cdot c_A$$

In addition makes it possible to interpret the corrected intensity as that which would be obtained for a theoretical medium having the same fluorescent element concentration c_A , but whose absorption parameters would remain constant and identical to those of the pure solvent (f' , f).

The corrected intensity method thus amounts to a transference of experimental results to this ideal medium in which all the calibration is linear by definition. Theoretically, therefore, a single experiment performed under the same conditions with a sample or standard U of known fluorescent element concentration γ_A will be sufficient to calculate the proportionality constant:

$$\frac{C}{f' + f}$$

according to the equation:

$$I'_{E_1} = \frac{C}{f' + f} \gamma_A \quad (6)$$

Thus the result is simply:

$$\frac{c_A}{\gamma_A} = \frac{I'_{E_1}}{I'_{U_1}} \quad (7)$$

From this one can see that only a single control sample was necessary to perform all the tests for a given element, provided that the dilutant always remains the same, however, since the

proportionality constant depends on the nature of the dilutant, by the term $(f' + f)$. It is also important to point out that all the concentrations or dilutions involved here must be understood as by weight.

It may be noted that the method summarized above is quasi-absolute, since it dispenses with any assumptions as to the nature and general composition of the unknown samples.

II. IMPLEMENTATION OF METHOD

II.1 Nature of Samples.

The samples involved here are doped oils and additives containing sulfur, phosphorus, calcium, barium and zinc. The addition of these elements to mineral oils in the form of organometallic salts is designed to improve the lubricating characteristics of these oils at high temperatures and their emulsifying properties so that they can be used to pick up and disperse solid deposits, calamine among others.

To check the validity of the proposed analysis by x-ray fluorescence, the samples were prepared by weighing and then mixing organometallic salts with pure mineral oils. The element contents were therefore known.

II.2 Preparation of Samples

a) Doped oils

The intensity I_{E_1} was measured from the initial product, and the intensity I_{E_2} from the same product diluted by its own weight in paraffin.

b) Additives

Here the procedure was the same as for the doped oils. Satisfactory results were obtained in regard to all the elements except zinc, which underwent much more pronounced absorption effects. For this element, measurement of the intensity I_{E_1} was performed on the product diluted with paraffin oil by a factor of 20, and I_{E_2} on the product diluted by a factor of 40.

II.3 Choice of Analytic X-Rays

All the elements with the exception of barium were measured with K_{α} x-rays. The use of a chromium anode tube led us to choose the L_{α} x-ray for barium, since the excitation of this wavelength by CrK_{α} emission is especially strong. Furthermore, the background is very slight at this wavelength, while the BaK_{α} x-ray coincides with the maximum white radiation emitted by the tube and scattered by the sample.

III. EXPERIMENTAL CONDITIONS

III.1 Presentation of Sample

Since the lower surface of the sample was irradiated, the choice of thin wall for the sample holder was of increasing importance for the measurement of lighter elements. A Mylar (polyethylene terephthalate) sheet 6 microns thick is ordinarily used. This material has two drawbacks: first, it is relatively absorptive of the long wavelengths of light elements (for PK_{α} , for example, the emissivity is only 40%), and second, the absorptive power varies widely due to the presence of unequally distributed traces of antimony in the polyester. For these reasons, we preferred to use polypropylene 6 microns thick, whose emissivity is higher than 80% for PK_{α}) and which has no heavy metal inclusions. These two characteristics make it possible to increase the sensitivity and decrease the effect of variations in the thickness of the wall on the measured intensity.

III.2 Experimental Conditions

These are given in Table I.

The use of germanium crystal is recommended for phosphorus determination, since it makes it possible to eliminate the second order CaK_{β} x-ray in the neighborhood of PK_{α} . However, it does require extremely precise adjustment of the amplitude discrimination to preclude background variations due to the GeK_{α} emission by the crystal.

TABLE I

Element	X-ray used for measurement	Excitation	Collimators	Analyzing Crystal	Detector
Phosphorus	PK _a	Chromium tube kV/40 mA	500 μ m	Germanium	FC (*)
Sulfur	SK _a	.	500 μ m	Pentaerythritol	.
Calcium	CaK _a	.	150 μ m	LiF (200)	.
Barium	BaL _a	.	150 μ m	.	.
Zinc	ZnK _a	.	150 μ m	.	SC (**)
(*) Gas flowmeter (**) Scintillator					

III.3 Background

In this study we have overlooked to the intensity of the background, which was generally slight, and have not subtracted it from the intensity measured with the measurement x-ray. As a result, the curves giving the variations in fluorescent intensity as a function of concentration do not pass through the point of origin.

IV.

IV. RESULTS

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The results obtained, illustrated by Figs. 1-8, are given in Tables II (doped oils) and III (additives).

IV.1 Interpretation

Since the elements sought were of known concentration, we measured the fluorescent intensities and calculated the corresponding corrected intensities, except in the cases of sulfur and phosphorus in the additives (see introduction) and for calcium in the doped oils, which could be measured directly due to its high level of dilution. /854

It may be observed that direct measurement generally results in a disordered intensity/concentration relationship, which precisely translates the existence of matrix effects, while in all cases the corrected intensities/concentration relationship was found to be appreciably linear, this being the purpose of the check performed,

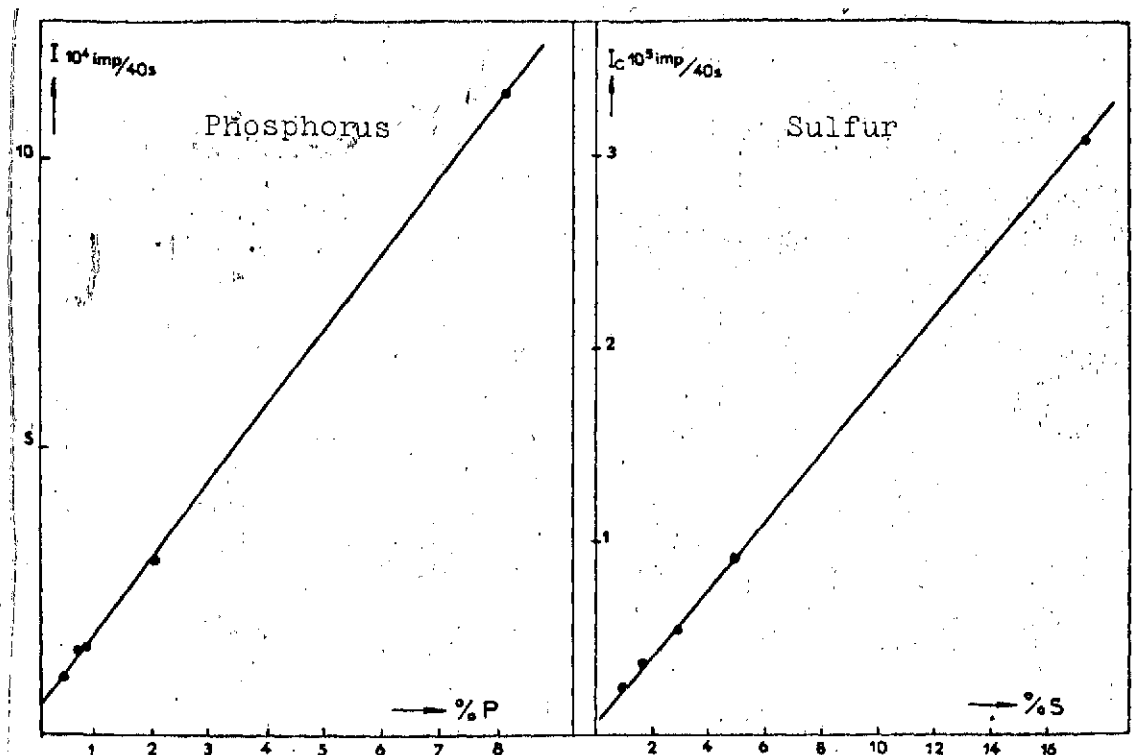


Fig. 1: Variations in fluorescent intensity as a function of concentration: direct measurement (additives diluted 20 to 1).

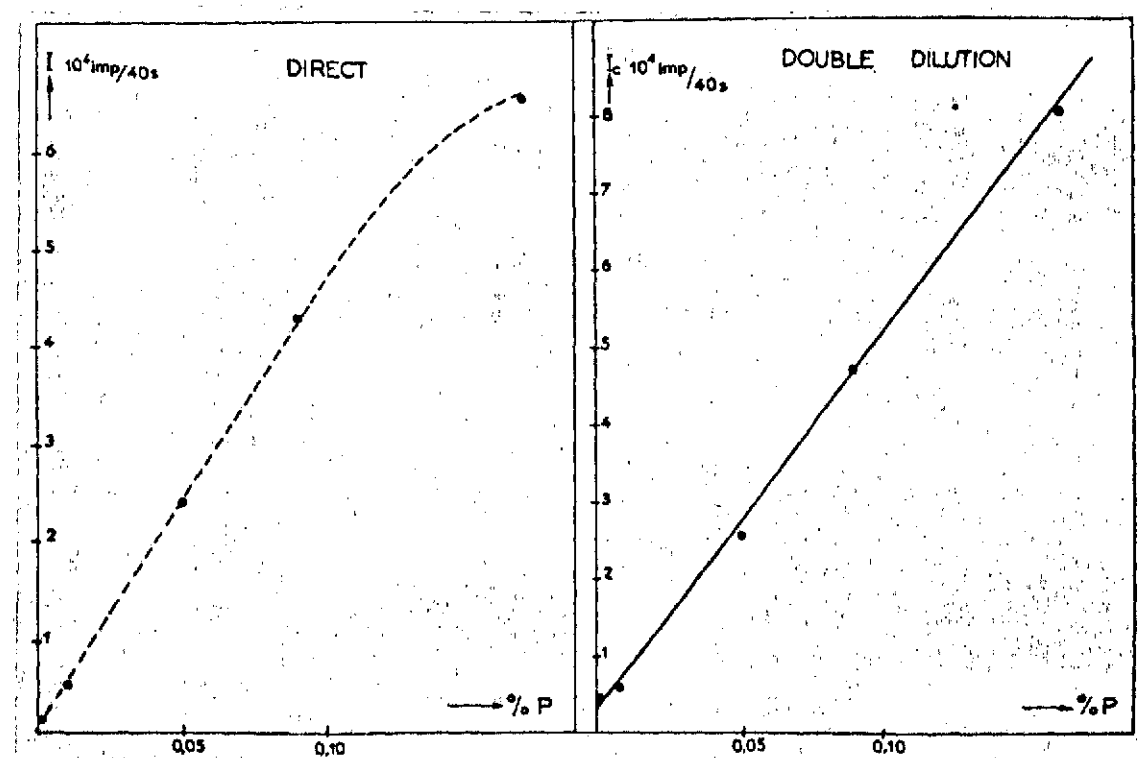


Fig. 2: Variations in fluorescent intensity as a function of concentration: phosphorus in doped soils.

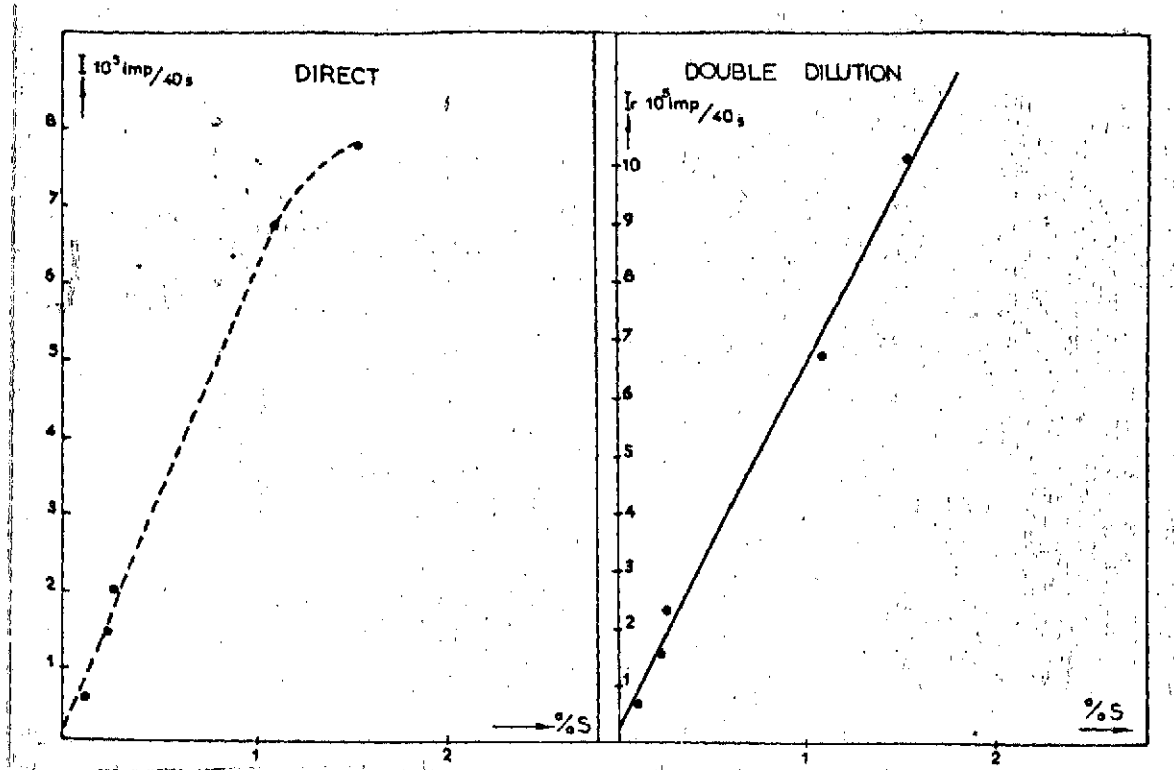


Fig. 3: Variations in fluorescent intensity as a function of concentration: sulfur in doped oils.

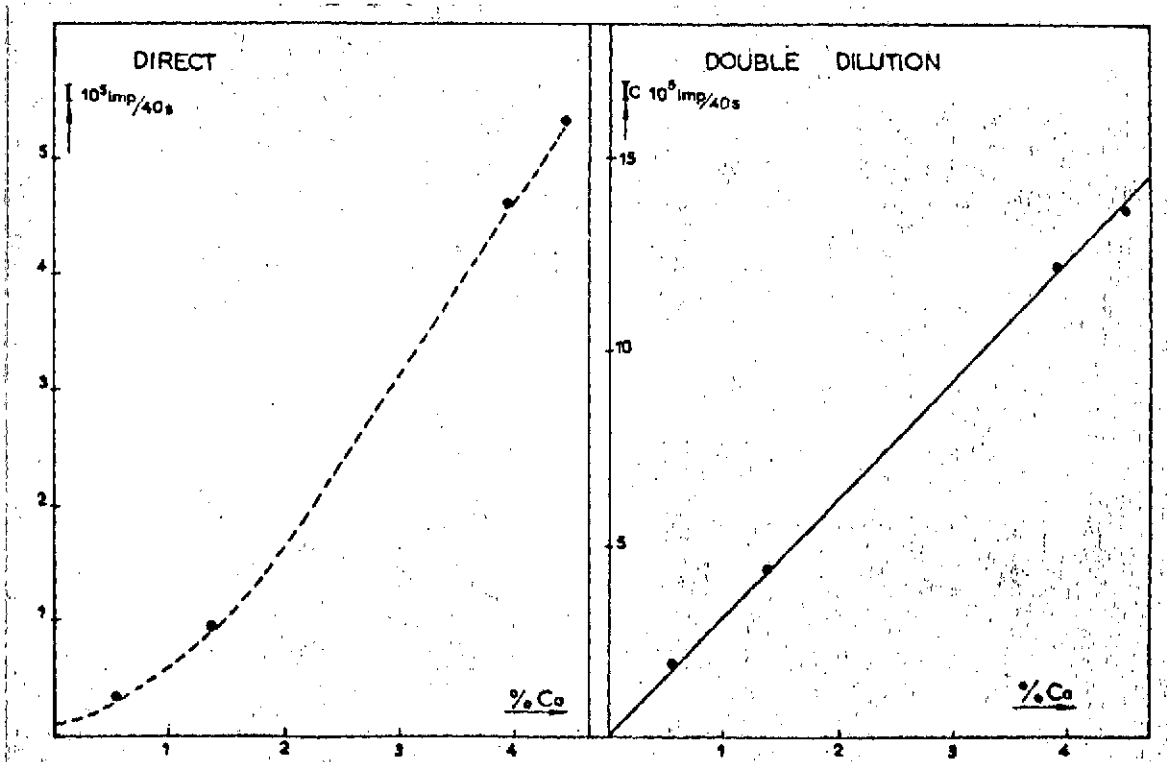


Fig. 4: Variations in fluorescent intensity as a function of concentration: calcium in additives.

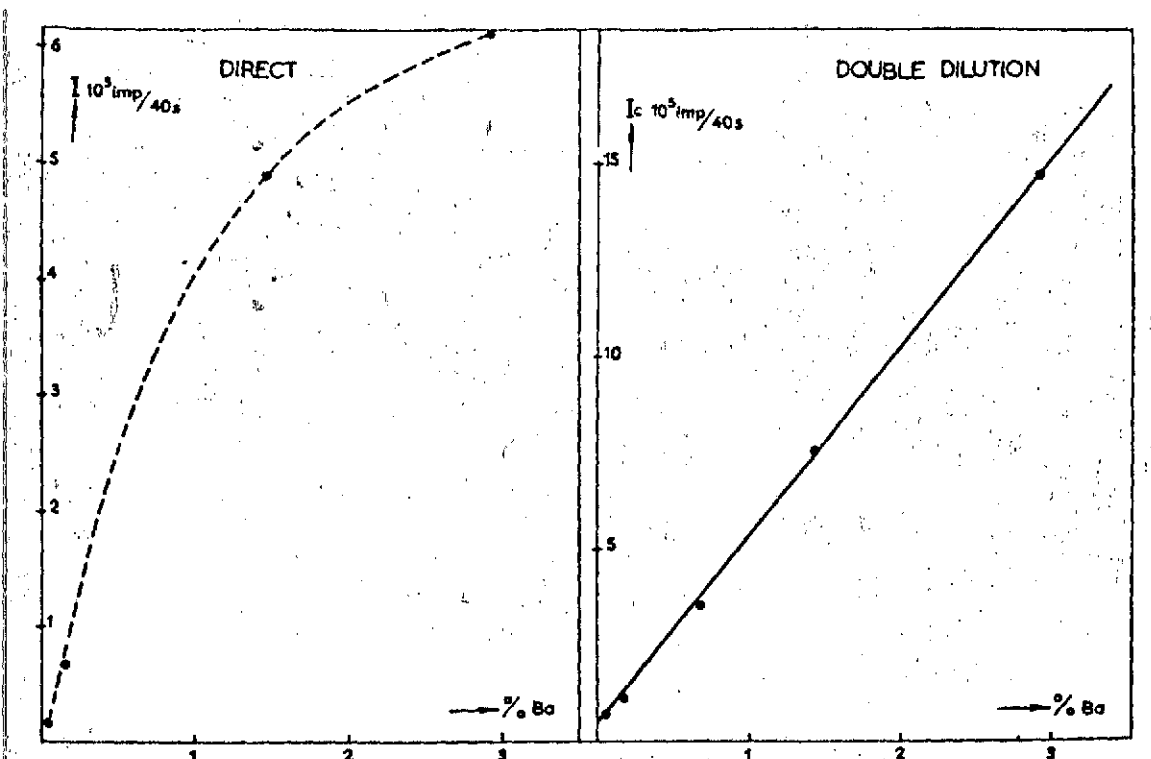


Fig. 5: Variations in fluorescent intensity as a function of concentration: barium in doped oils.

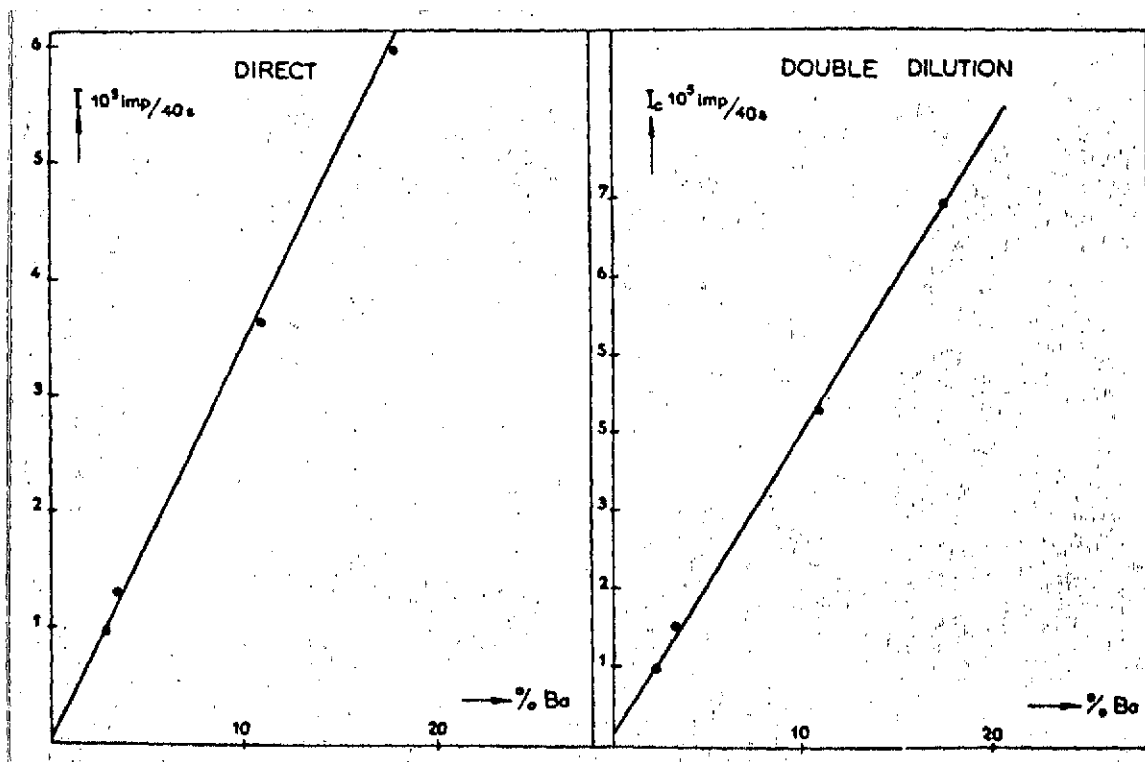


Fig. 6: Variations in fluorescent intensity as a function of concentration: barium in additives.

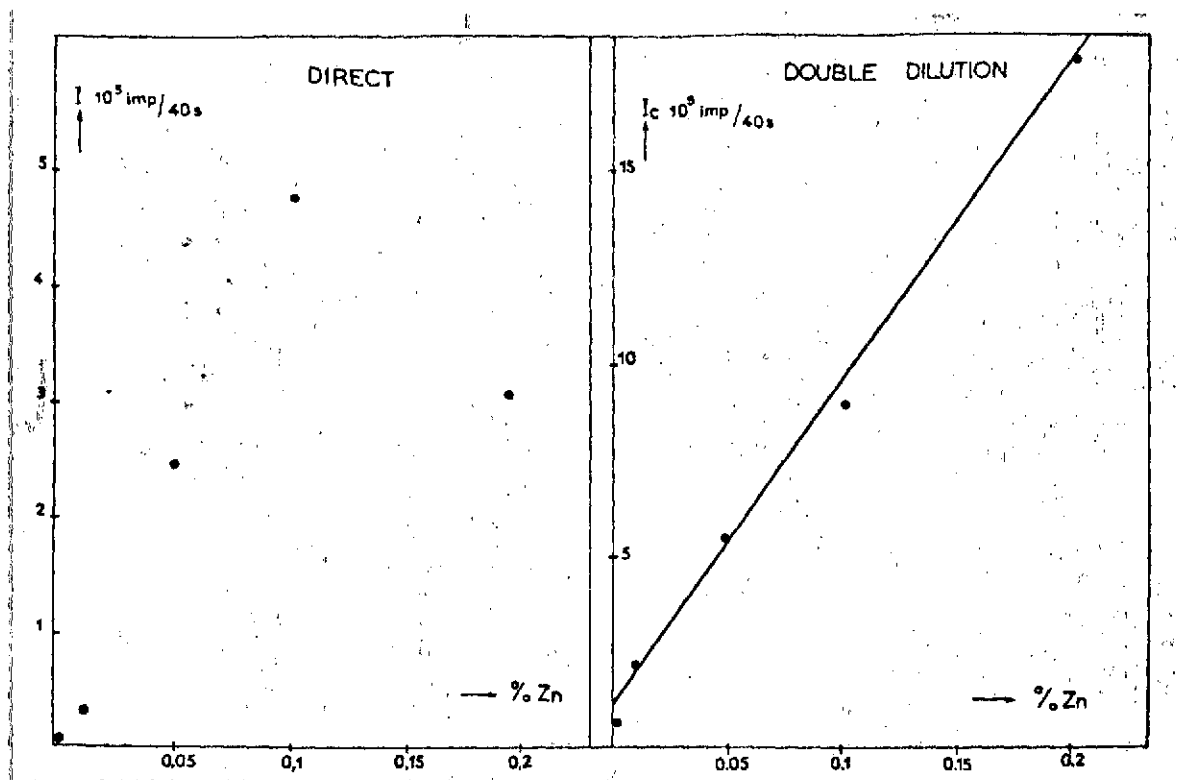


Fig. 7: Variations in fluorescent intensity as a function of concentration: zinc in doped oils.

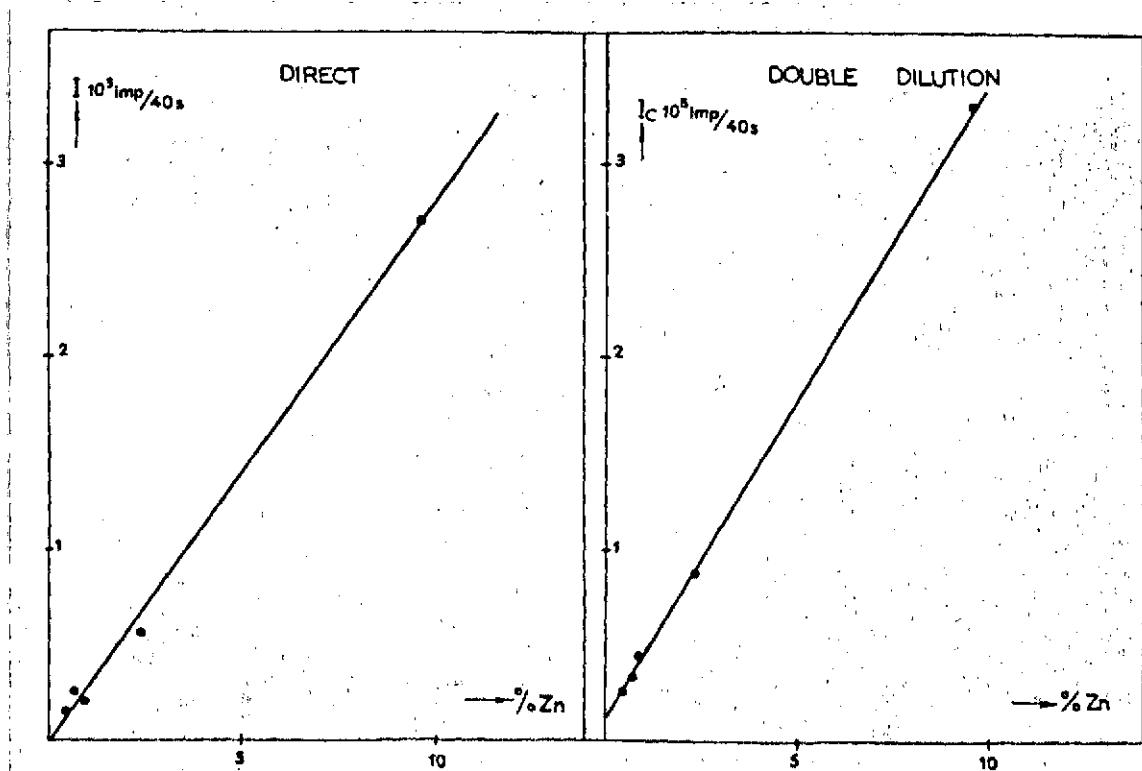


Fig. 8: Variations in fluorescent intensity as a function of concentration: zinc in additives diluted 20 to 1.

TABLE II: DOPED OILS

Element	Sample Number	Fluorescent Intensity (in thousands of counts in 40 sec)		Corrected Intensity	Actual Concentration (%)	Theoretical concentration (%)	Absolute Difference	Relative Difference (%)
		I_{x_1}	I_{x_2}					
Ba	1	64.96	42.02	119.0	0.154	0.15	0.004	2.3
	2	617.60	434.90	1470.1	2.88	2.90	0.02	1
	3	487.33	294.60	744.9	1.45	1.42	0.03	2.1
	4	21.43	16.98	80.3	0.037	0.047	0.01	20
	5	163.25	111.49	350.9	0.648	0.64	0.008	1.2
Ca	1	65.02	direct measurement	direct measurement	0.168	0.170	0.002	1.2
	2	30.20			0.054	0.054	0	0
	3	18.48			0.0199	0.020	0	0
	4	27.66			0.857	0.860	0.003	0.35
	5	699.60			2.240	2.24	0	0
Zn	1	243.50	164.70	509.0	0.05	0.052	0.002	4
	2	313.20	266.00	1765.0	0.195	0.195	0	0
	3	20.20	10.10	20.4	0.002	0.0015	0.0005	20
	4	474.20	308.20	880.0	0.102	0.096	0.004	4
	5	29.60	26.03	213.7	0.0097	0.017	0.0073	8
S	1	669.60	334.76	669.3	1.11	0.97	0.04	4
	2	773.90	445.80	1051.5	1.55	1.55	0	0
	3	201.80	106.10	223.8	0.27	0.32	0.05	15
	4	147.60	77.05	160.9	0.239	0.23	0	0
	5	65.90	34.20	70.6	0.114	0.095	0.009	10
P	1	23.97	12.35	25.3	0.047	0.047	0	0
	2	66.29	36.44	80.8	0.162	0.16	0	0
	3	1.61	1.22	4.8	0.0018	0.0016	0.0002	11
	4	42.89	22.54	47.4	0.085	0.092	0.007	11
	5	4.98	2.74	6.0	0.008	0.007	0.001	14

TABLE III: ADDITIVES

Element	Sample Number	Fluorescent Intensity (in thousands of counts in 40 sec)		Corrected Intensity	Actual Concentration (%)	Theoretical concentration (%)	Absolute Difference	Relative Difference (%)
		I_{x_1}	I_{x_2}					
Ba	1	90.30	46.30	95.1	2.31	2.15	0.16	7.5
	2	362.00	196.10	427.8	10.80	10.60	0.20	0.9
	3	598.00	322.00	698.0	17.28	17.50	0.22	0.12
	4	129.00	68.40	146.1	3.24	3.50	0.26	7.5
	5							
Ca	1	464.40	335.80	1212.0	3.92	3.94	0.02	0.5
	2	90.00	74.60	432.5	1.40	1.40	0	0
	3	35.44	29.58	177.0	0.56	0.54	0.02	3.5
	4	535.60	385.20	1372.0	4.48	4.48	0	0
Zn	1	25.47	14.52	33.7	0.75	0.70	0.05	6.6
	2	58.22	35.11	88.4	2.44	2.42	0.02	0.8
	3	22.48	14.90	44.5	0.97	1.00	0.03	3
	4	16.93	10.41	27.0	0.49	0.50	0.01	2
	5	269.64	148.50	330.1	9.75	9.75	0	0
S	1	39.06	direct measurement	direct measurement	1.84	1.80	0.04	2.2
	2	91.85			5.01	5.00	0.01	0.2
	3	55.15			2.81	2.80	0.01	0.35
	4	24.91			1.12	1.10	0.02	1.8
	5	309.70			17.3	17.30	0	0
P	1	14.03	direct measurement	direct measurement	0.70	0.68	0.02	3
	2	30.13			2.02	2.00	0.02	1
	3	15.04			0.81	0.80	0.01	1.2
	4	10.34			0.40	0.40	0	0
	5	111.93			8.09	8.10	0.01	0.12

The advance made in this way is especially valuable in regard to the measurement of barium in doped oils (Fig. 5), zinc in doped oils (Fig. 7) and calcium in additives (Fig. 4), since in these cases the matrix effects are greater. The advance is also significant in the /855 determination of phosphorus and sulfur in oils (Figs. 2 and 3) and zinc in additives (Fig. 8).

In cases in which direct measurement reveals a linear intensity/concentration relationship, i.e., when the matrix effects are not appreciable, it is useless to calculate a corrected intensity since this will be marred by algebraic error due to the accuracy of measurement, which may be greater than the correction to be performed if the latter is extremely small.

IV.2 Drawbacks of Method

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This method requires two preparations per analysis, and at least one of these necessitates two precise weighings. In addition, optimization of the measurements by the choice of a suitable dilution ratio and concentration range implies preliminary measurements which proportionately increase the total time required for the procedure. Finally, with equal theoretical error, the determination time itself will be more than twice that of a direct method of determination.¹

IV.3 Advantages of Method

Since the proportionality of the corrected intensities and the concentrations has been established, the user can dispense with systematic calibration while at the same time using a technique which

¹ Simple theoretical calculation does not make it possible to relate the standard differences in regard to the measurements of I_{E1} and I_{E2} to the standard difference in regard to I'_{E1} since the Y distributions resulting from the combination:

$$Y = \frac{Y_1 \cdot Y_2}{Y_2 - Y_2} \quad [\text{sic}]$$

in which Y_1 and Y_2 are two normal gaussian distributions, is not a gaussian distribution of the same type.

ensures satisfactory reproducibility.

To measure the concentration of a given element in a random sample, one need only prepare a standard containing a known quantity of this element. To measure the concentration, four determinations will be necessary, that is:

- one determination performed on the sample to be analyzed and another on the sample diluted at a suitable ratio in a neutral solvent;
- one determination performed on the standard and another on the standard diluted in the same solvent as the sample.

The concentration ratio may be derived from the ratio of the corrected intensities calculated from these measurements.

Applied to the analysis of hydrocarbons, the method offers the following advantages:

- simplicity of use: one standard prepared once and for all by dissolving salts of different elements (naphthenates in particular) can be used to measure these elements in turn;
- reproducibility of measurements: the standards are used as a reference for adjustment of the assembly. In this way the deviation can be systematically corrected;
- general applicability: the method can be used in a general manner to measure the concentrations of mineral elements in hydrocarbons without any concern for possible variations in the absorptance of the sample (differences in the C/H ratio, inopportune presence of absorptive mineral elements) -- unless this is desired in order to determine the optimum conditions for analysis.

CONCLUSION

The use of x-ray fluorescence spectrometry seems to be well-adapted to the problem of measuring the concentrations of mineral elements in hydrocarbons, provided that the method of corrected intensities by double determination at two dilution ratios is used. In our opinion, this method provides a definite advance, especially in cases of heavy mineral element concentrations, where

interelement effects are considerable, since it is the only method which makes it possible to limit the final relative error to an acceptable level on the order of 1%.

The purpose of this research has been to apply this method to liquid samples to check the validity of the theoretical assumptions, especially that regarding the incorporation of the primary radiation into an equivalent monochromatic radiation; so far these assumptions have been verified only for solid solutions [3,5]. The results were positive, as was illustrated especially by the results obtained in the determination of zinc (Figs. 7 and 8), whose ZnK_{α} x-ray is excited solely by the white radiation of the chromium tube, that is, an essentially polychromatic spectrum.

Since this article was written, R. Tertian has established [7] that the relative theoretical error introduced by the polychromatic structure of the primary radiation is extremely slight and is no more than 0.5% in all usual cases, in which the essential consideration is absorption phenomena. It may be slightly higher (maximum of 1-2%) if there are extremely heavy enhancement effects; however, this would seldom occur in practice in solutions analysis. Based on these new developments, one can generally expect a degree of accuracy on the order of 0.5 to 1% as a relative value, provided, however, that the preparation and the determinations are rigorously correct.

A considerable improvement can therefore be made in our initial results by setting up optimum conditions of analysis for each element and each matrix. These problems will be examined in a future optimization study.

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